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INFLUENCE OF THE ILLUMINATION OF A NON-IONIC SURFACTANT USED FOR THE DISPERSION OF OIL SPILLS AT SEA

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Environmental Protection Agency
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[Influence de l'éclairement sur la biodégradation d'un Tensio-Actif non ionique utilisé pour la dispersion des nappes de Pétrole en mer]

Jean-Claude Lacaze

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16. Abstracts

MARINE MOLYSMOLOGY - Influence of the illumination on the biodegradation of a non-ionic surfactant used for the dispersion of oil spills at sea. [1] Note (*) by Mr. Jean-Claude Lacaze, introduced by Mr. Maurice Fontaine.

The influence of the illumination is usually neglected in the assays of biodegradation. It is this parameter that we study in this paper, and its action on the biodegradation of a non-ionic surfactant. The results of these preliminary studies indicate that even a very weak illumination can slow down the biodegradation.

In the frame of our studies on the biological effects of the petroleum and adjuvants mixed to it in order to favor its dispersion and biodegradation, we have been led to examine the problem of the biodegradability of these pollutants. We present here the study of the influence of various illuminations on the biodegradation of a non-ionic surfactant: the nonylphenol with nine molecules of ethylene oxide. This product, of which domestic and industrial consumption reach large amounts, is a component of many agents dispersing the hydrocarbons such as Gamosol; on the other hand, we analyze its effects on the marine microflora [9 to 12].

17. Key Wo

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Tanker ships
Petroleum Industry

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I. Experimental Protocol

The water and the sediments necessary to this study were collected in November, 1970, in a lagoon environment of one of the many ponds of the County of "Olonne Isle", close to the city of the Sables-d'Olonne. This pond, like all those on the Atlantic Coast, is under an indirect influence of the tides by a system of locks and channels; by this system the brackish-waters ponds are filled during the high tides. The drainage periods — of lengths regulated by the oyster breeders — are usually not longer than a few days, which allow the cleaning of the pools.

(*) Session of June 25, 1973.

We harvested our specimens in a flat bottom pond, very homogeneous and shallow (30 to 40 cm), used for the maturing of the oysters. The sediment is obtained during a drainage period by scraping of the first 3 centimeters of the surface; it is homogenized, then spread at the bottom of large 4-liter glass beakers, about 400 g per container. Three liters of water are poured in each beaker a few hours later, at the time when the pond is filling up. We used 30 beakers containing as many similar experimental media as we will put under different experimental conditions. This type of ecological research has been called "microcosmic method" [13] because of the small size of the established media (micro-ecosystems) and of their isolation from the rest of the biosphere. We will not describe here the use of experimental ecosystems for the Molysmology [4] or science studying pollutions; these data were already published by Fontaine and Lacaze [5].

Two series of beakers are prepared: 15 are polluted by 20 mg/liter of nonylphenol; 15 by 40 mg/liter of the same. To 8 beakers of each series is added (50 ml/liter): an extract of sediment made from the slime of the pond (an equal weight of superficial sediment and sea water are autoclaved. After decanting, the supernatant is filtered, sterilized and stored in the cold), then $NaNO_3$ (200 mg/liter) and Na_2HPO_4, $12H_2O$ (30 mg/liter). Out of the 30 beakers, 22 then undergo a period of 14 days of various experimental conditions in several climatic atmospheres where the illumination, photoperiod and temperature are regulated. The 8 beakers left over are disposed in situ on submerged supports so that the pond water fills them up to 2/3 of their height. The water and sediments of the containers are then under the conditions of lighting and temperature normal to a month of November. The table indicates each of the 15 experimental conditions established for one or the other series of 20 or 40 mg/liter. The ecosystems chosen to demonstrate the biodegradation in the dark are protected from the light by an opaque plastic sheet. The nonylphenol is titred on the 4th, 9th and 14th day after pollution by the technique of Greff, et al [7], which is based on the formation of a blue complex between the alkylphenol oxyethylene chains and an ammonium cobalt-thiocyanate reagent, salted out in a saturated NaCl solution, and extracted

by benzene which optical density is read at 320 mμ. The results of biodegradation are expressed in percentage of the initial titer.

II. Results

Both series of ecosystems — respectively 20 and 40 mg/liter of surfactant — show similar kinetics of biodegradation, so that for clarity's sake we have indicated only the results of the 20 mg/liter series on the Figures 1 and 2; the data obtained later on for this series could be extrapolated to both the series.

The diagrams 1c and 1d (Figure 1) demonstrate that at a 20° C temperature, obviously the illumination retards the biodegradation. The quantity of pollutant present in the medium is then important: if the medium is enriched (1d), an important initial inhibition of the biodegradation by the light is observed; however, at the end of the experiment, the concentrations in nonylphenol are similar in the lighted and darkened ecosystems. On the other hand, if the medium is not enriched (1c), the biodegradation is blocked after an incubation of 9 days. Those results seem to indicate that there is competition for the nutrients between the algae-microflora, and the bacteria responsible for the destruction of the nonylphenol. The light favors the growth of the algae at the prejudice of the bacteria. It is also possible that the algae secrete a bacteriostatic substance in the medium (2). The incidence of the illumination is important, even if the luminous energy is low and of short duration; for a photoperiod of 6 hours, and a weak illumination of 1200 lx, we observe a biodegradation 54% lower, compared to the percentage in the darkness (1d). The figure 1d indicates also that above a certain threshold of illumination, there is no more proportionality between the luminous energy provided to the ecosystems, and the slowing up of the biodegradation.

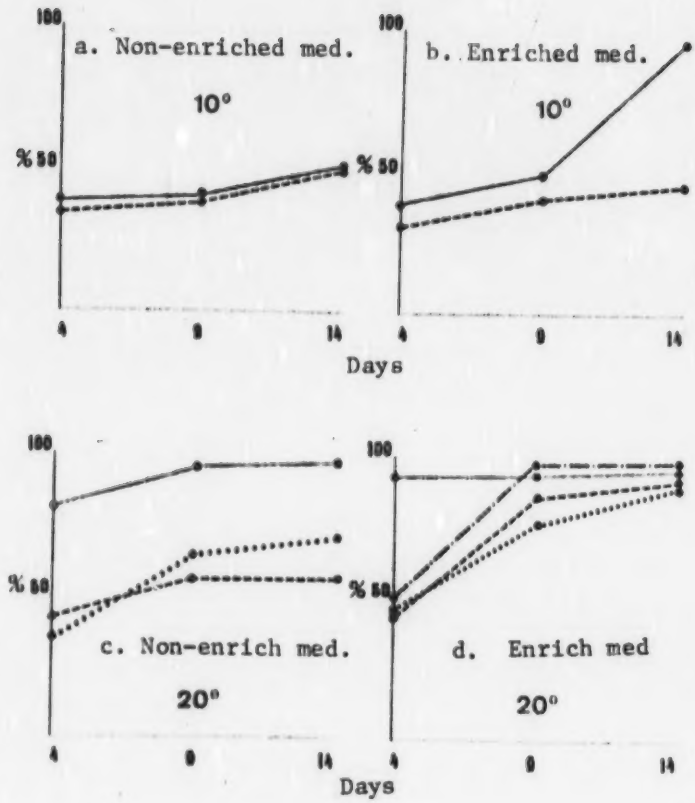
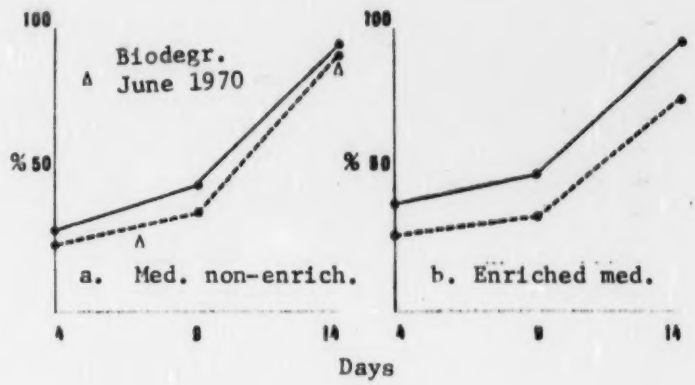


Figure 1. Percentage of biodegradation of nonylphenol in the laboratory as a function of time.

Lower temperatures (10° C., Figure 1a) are a limiting factor. Then the presence of nutrient favors only slightly the destruction of the pollutant (1b). These remarks are also valid for the in situ assays (Figure 2). Those being performed during a cold season (November), the kinetics of biodegradation of the nonylphenol are similar to those observed in laboratory at 10° C (Figure 1a-b). However, at the end of the experiment, a greater biodegradation is observed in the natural-conditions environment. The longer photoperiod (12 hours) in the laboratory must then constitute a limiting factor.

It is also useful to compare the results obtained in situ in November to those obtained in June (Figure 2a) in a previous work [11]. Though the ecological conditions are different, the kinetics of biodegradation are similar in June and November. Those results, which appear at first as paradoxical, can be explained if one considers that biodegradation is the result of two factors acting in opposite ways, temperature and illumination. In November, the low temperatures are disadvantageous to the destruction of the nonylphenol, but the weak illumination is negligible. In June, the opposite reaction is observed.



—— Biodeg. in dark ---- Natural light

Figure 2. Percentage of biodegradation of nonylphenol in situ in function of time.

TABLE. EXPERIMENTAL CONDITIONS OF THE BIODEGRADATION OF NONYLPHENOL ILLUMINATION EXPRESSED IN HOURS PER 24 HOURS. THE LIGHT INTENSITY IS 1200 lx FOR THE 6 h PHOTOPERIOD, AND 2600 lx IN THE OTHER CASES.

		temperature	Illumination (1)			
			0	6	12	24
Lab Assays	Non-Enrich. media	10°	+	−	+	−
		20°	+	−	+	+
	Enrich. med.	10°	+	−	+	−
		20°	+	+	+	+
Assays in situ	Non-enrich. med.	Natural	+	Natural		
	Enrich. med.		+	Natural		

III. DISCUSSION AND CONCLUSION

Illumination plays a very important part, especially if the temperature is not a limiting factor. The slowing up of the biodegradation by light seems particularly obvious when the medium is poor in nutrients (Figure 1c). The ecological consequences of these observations are remarkable. Certain factors which selectively retard the growth of algae by restricting the light, such as water turbidity or the presence of an emulsion of hydrocarbons on the surfaces, can also favor the biodegradation. The petroleum oils and by-products, by attenuating the passage of light, could, by the same token, favor the destruction of their incorporated dispersant-products, and maybe even — though still to be demonstrated — their own destruction.

Nevertheless, an eventual retardation of the light is not necessarily detrimental to the equilibrium of the polluted ecosystems. A rapid biodegradation, which necessitates large amounts of oxygen in a short time, can be harmful to the life of many organisms. In fact, in the case of natural

purification, there must be an equilibrium between the organisms responsible for the destruction of the pollutant.

For the application of treatment of certain residual waters, the illumination can have an important incidence as far as the purification is concerned; the algae are able to slow up the purification so that their growth must be limited at the maximum. In the case of the aeration of the lagoons, for instance, the depth of the pools and the turbidity by stirring could be increased in order to diminish the light.

We can also ask the following question: to what extent are the measures of biodegradation in laboratory representative of the biodegradation in natural environment? The assays used to measure the rate of biodegradability of pollutants are performed in experimental conditions which are remote from the natural environment in order to simulate, generally, a purification station; the medium rich in organic matter is then enriched by a microflora adapted to the pollutant. Also, the conditions of illumination are rarely clarified [3]. But if it is necessary to know the rate of biodegradation in the purification stations and in the polluted waters, and by then in systems having a more or less developed microflora adapted to the pollutant, it is equally important to know the rate in natural environments having never been polluted [6, 8]; in this case the factor "illumination" is susceptible to play a non-negligible part. This is what led us to study in this work the kinetics of biodegradation of the nonylphenol with 9 ethylene oxide molecules, in some ecosystems not adapted to this pollutant.

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